UV Curable High Opacity Ink Jettable White Ink

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Abstract:

An opaque white UV curable inkjet ink is a critical component for printing in graphic arts and industrial digital printing markets since materials such as transparent films and dark pre-colored surfaces are used extensively. Properties such as high opacity and settling stability are an important prerequisite when used in a piezoelectric printhead. However, the large density difference between inorganic pigments and the ink vehicles leads to problems associated with settling. This paper discusses white inks that have high opacity, good settling stability, excellent end user properties and jet stability.

Introduction

The printing industry has witnessed great strides in the advancement of inkjet inks. Technological progress has extended the application of inkjet printing into the realm of wide-format printers and beyond.[1] Although several types of printing processes such as screen printing, offset printing, digital photo imaging and thermal transfer are known, inkjet technology provides a definite edge. To highlight a few, the ability to be used in different printhead technologies, tailor end user properties based on the ink and carrier media, makes inkjet very attractive. The technology enables quick response to custom prints that can reduce expense on prepress process coupled with less ink wastage. Inkjet technology is emerging as a leading digital imaging method for a variety of industrial applications such as graphic art, packaging, decorative and display device fabrication and for security purposes and for tracking systems.[2]

UV Inkjet

New developments in print heads have enabled use of energy curable inks, whereby UV light provides rapid curing upon transfer of the ink on to the substrate. UV curable jetting chemistries are rapidly emerging as the next key enabler for piezo drop-on-demand (DOD) ink jet technology.[3] UV curable inks offer significant advantages over solvent based inks, which include absence of volatile organic compounds (VOC), fast cure and low energy requirement, good chemical and solvent resistance, high gloss and vibrant colors. Furthermore, printhead nozzles can be left uncapped for long periods of time as they do not have solvents thereby reducing nozzle blocking which leads to significantly low rate of nozzle failure.

Although UV curable inks of a full process color system is relatively easy to formulate, a white UV curable ink is a real challenge. Herein we highlight a jettable UV curable white ink of high opacity and pigment loading with good settling stability.

Challenges for UV Curable White InkJet Ink

UV curable white ink needs to satisfy several requirements. Some of the important properties include viscosity, surface tension, particle size, settling stability, opacity for the cured film, cure speed, adhesion to several substrates, and jet stability, i.e. low nozzle failure.

Formulating an ink with the above requirements is a real challenge since some of them represents antagonistic relationship between performance and physical properties. Because of the small droplet size fired from DOD printheads, inks must be of low viscosity, which requires the use of monomers and low viscosity oligomers. However, a high opacity white ink also requires a high loading of inorganic pigments such as TiO_2 and ZnS or a combination thereof. Due to the density differential between the monomer and the inorganic pigments, rapid settling is very much an inherent problem in these inks. Hence, settling and supernatant formation are unavoidable but the speed at which this occurs is sensitive to the components present in the ink.

Ink Properties

Viscosity

Viscosity plays a crucial role during the printing process and must be optimized to ensure maximum reliability and high print quality. The white ink has a viscosity range of 10–14 cps at jetting temperatures, which makes it an excellent candidate for piezoelectric printheads. Figure **1** shows a representative temperature/viscosity curve for the white ink. Based on the high shear rheology experiments, the change in viscosity at the jetting temperatures is relatively minimal, permitting reliable jetting over a wide temperatures range.

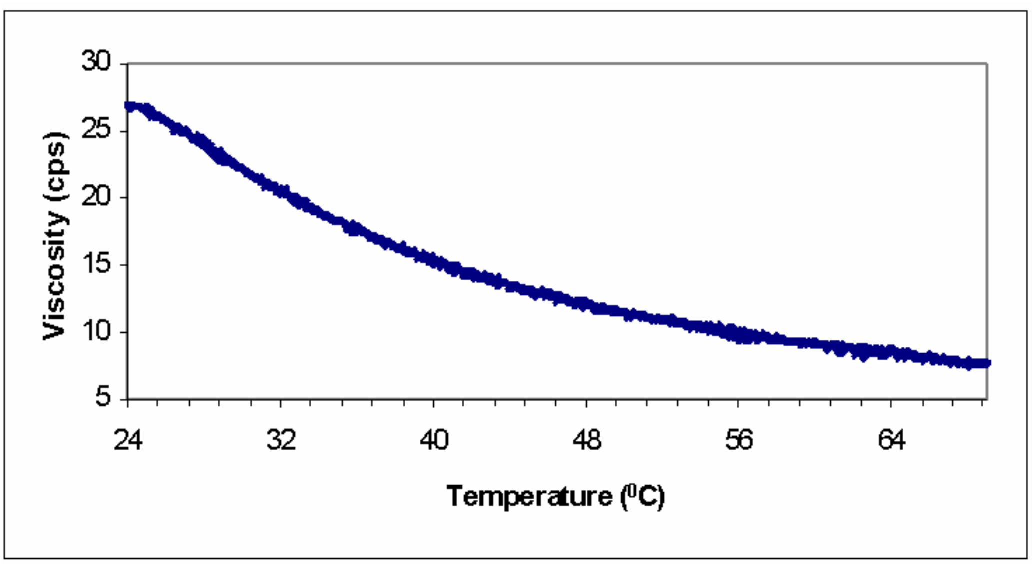

Figure **1**. Viscosity-temperature curve for the white ink.

Surface Tension

Surface tension is an important property in relation to ink-jet technology. The surface tension dictates the position of the ink meniscus within the nozzle along with drop quality. Ink with too low a surface tension will result in excessive nozzle face plate wetting, which can impact jet reliability due to reduced ink ejection. Conversely, high surface tension can hinder droplet ejection due to insufficient wetting of printhead nozzle. Furthermore, the surface tension of the ink is also critical for substrate wetting. Static/equilibrium surface tension was measured by Wilhelmy plate method using a Kruss Tensiometer K100. The equilibrium/static surface tension is optimized in the range of 24-28 mN/m so as to provide good wetting characteristics both within the printhead and over a wide variety of substrates.

Dynamic surface tension which measures the rate at which bubbles are formed was determined using a Kruss BP2 Tensiometer. The technique involves measuring the surface tension by varying the surface age for the sample from 10 to 50000 msecs. Gas is bubbled through a capillary immersed in the liquid and the bubble pressure related to surface tension at maximum radius (radius of the capillary tip) is measured. The technique was used to investigate the correlation between surface tension and jetting. However, it is known that jetting occurs in microsecond timescale, whereas the lowest surface age measurable with the instrument is 5-10 msecs. This surface age range relates to the inflight timeframe wherein ink drop has ejected from the printhead nozzle before reaching the substrate. Longer surface ages of around 500-1000 msecs relates to the timeframe wherein the ink drop has reached the substrate.

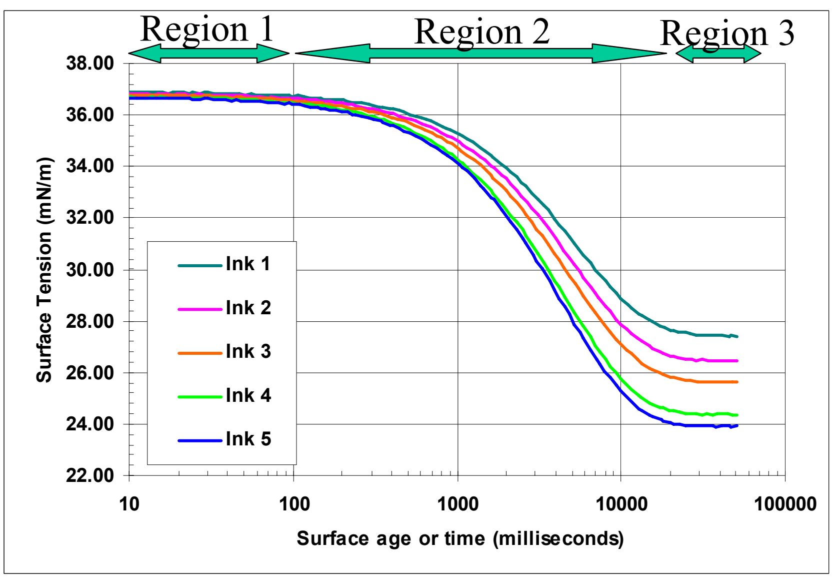

Figure **2.** Dynamic surface tension plots for white inks with different levels of surfactant.

The effect of concentration of the surfactant on dynamic surface tension of the ink was studied. Table **1** lists white inks with various levels of Byk 3500 surfactant, and Figure **2** shows the dynamic surface tension curves for those inks. The dynamic surface tension curve can be divided into three parts. The first equilibrium state (Region 1) represents values at low surface age, next a rate limiting stage (Region 2) and lastly a second equilibrium state (Region 3) represented by the static surface tension at high surface age. Ideally, at low surface age the ink should actually start to show a surface tension drop followed by a rapid drop. At longer time scale of up to 500 milliseconds the ink should reach an equilibrium value, which essentially happens to be the static surface tension. After reaching this value, it is not expected to change further. All three stages, described above will largely be dependent on the type of surfactant and its migratory process at different time scales after the moment the ink is fired from the printhead.

Sample	Amount of Byk3500 (ppm)	Wilhelmy Measured Equilibrium Surface Tension (mN/m)	σ_{eq} Calculated Equilibrium Surface Tension (mN/m)	$\Delta\sigma$ (mN/m)	Rate Constant k (milliseconds)
Ink 1	0	27.36	27.40	9.48	5344
Ink 2	50	26.38	26.42	10.40	5090
Ink 3	100	25.58	25.61	11.16	4881
Ink 4	250	24.32	24.35	12.35	4556
Ink 5	500	23.85	23.88	12.79	4434

Table **1**. Tabulated values of static surface tension and kinetic rate constants at various surfactant concentrations

Addition of Byk3500 surfactant results in a drop in the static surface tension of the ink as shown in the equilibrium surface tension values measured by the Wilhelmy method (Table **1**). The drop is more rapid with increasing amount of surfactant. The time scale for drop in dynamic surface tension is in the range of 100 to 20000 msec. The inks with about 250 and 500 ppm surfactant have a more rapid drop in surface tension in the same range.

A first order exponential decay fit was done to the data sets for all plots. The fits were made according to the following equation:

$$\sigma_t = \sigma_{eq} + \Delta\sigma \exp(-t/k)$$

where $\sigma_t =$ the surface tension at any given time, σ_{eq} = the calculated equilibrium surface tension, $\Delta\sigma$ = the decrease in surface tension over the time frame of testing, t = time, and k = the rate constant for the first order decay.

The values were determined and listed in Table **1**. The $\Delta\sigma$ values decrease with a decrease in the amount of surfactant since the overall decrease in surface tension ($\Delta\sigma$) decreases with increasing equilibrium surface tension. This is because the starting (10 millisecond) surface tension for each of the samples is very similar *ca.* 37 mN/m.

Bubbles formed during the process reach a maximum radius before being released from the capillary. The surfactants present in the ink diffuse to and come to equilibrium at a developing surface. The kinetics of this process follows a first order decay and the rate constant to equilibrium (k) decreases as the amount of surfactant increases to about 250 ppm. Further increase in surfactant concentration, does not lead any significant change in the rate. The rate-limiting step (changes in surface tension) is typically at much larger time scale for inks without surfactant.

Jetting Performance

In conjunction with jetting reliability, the ink was investigated using an Optica X Plus vision system (Xennia Technology Ltd.). This system allows for the droplet breakup visualization as it is ejected from the faceplate. An individual nozzle of the faceplate ejecting droplets over a range of strobe delays is examined. The strobe allows one to see droplets in flight. The white ink was examined with this system and the image is depicted in Figure **3**. It is evident from Figure **3** that the ligaments which are formed upon ejection from the nozzle combine with the drop to form an image without any satellites. The ink trajectory was straight and the nozzles showed no sign of failure. The ink maintains optimum faceplate wetting to allow efficient drop break up.

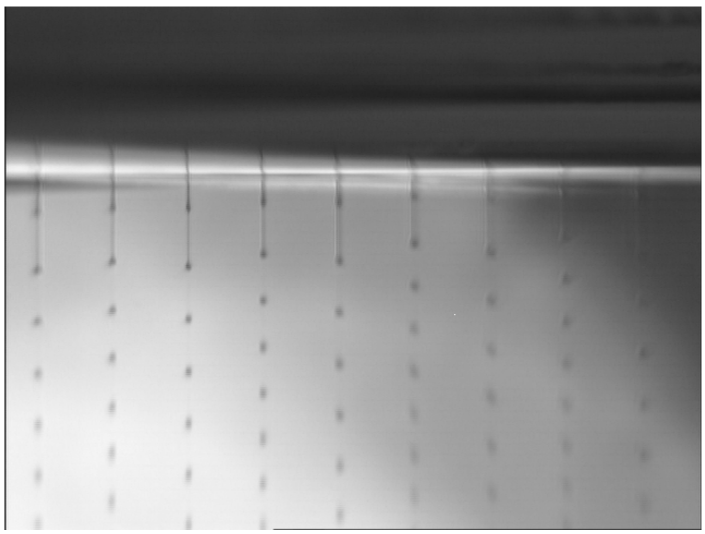

Figure **3**. Drop formation image of white ink from the Spectra SE-128 printhead at a firing frequency of 16 kHz, at 100V, and at 30ºC.

Cure Speed

A white ink is usually formulated to provide high opacity which requires a high pigment loading. However, this in turn can drastically affect the cure speed especially the bottom cure. This is because TiO_2 is a strong absorber of UV light.

A 9 micron thick coating of the ink was cured using a medium pressure doped mercury (Hg) vapor lamp powered at 300 Watts per inch. Cure speed was determined using FTIR by measuring the peak area at 810 cm^{-1} for the ink and the cured film. A plot of cure speed versus energy density or dosage for the white ink is shown in Figure **4**. The inks were formulated such that the cure is >90% for both top and bottom surfaces at and above a energy density of 200 mJ/cm^2.

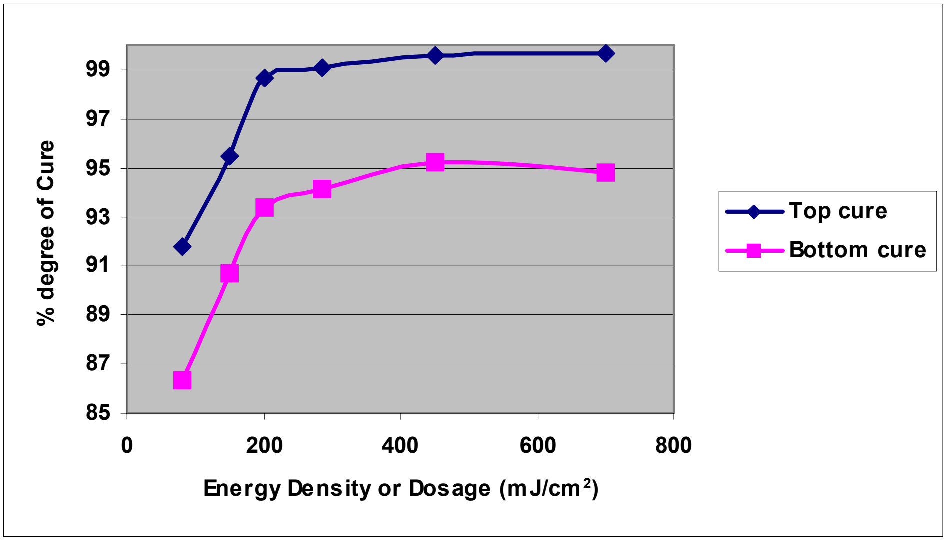

Figure **4**. Plot of % degree of cure versus energy density or dosage for the white ink.

Opacity

Inorganic pigments such as TiO_2 are commonly used as pigments in UV curable white inks. The particle size of TiO_2 plays a significant role in the opacity. Figure **5** shows the relative scattering power of red, green and blue light versus the particle size of TiO_2. It is evident that scattering of the red, blue and green light is maximized at a particle size of 200-300 nm.

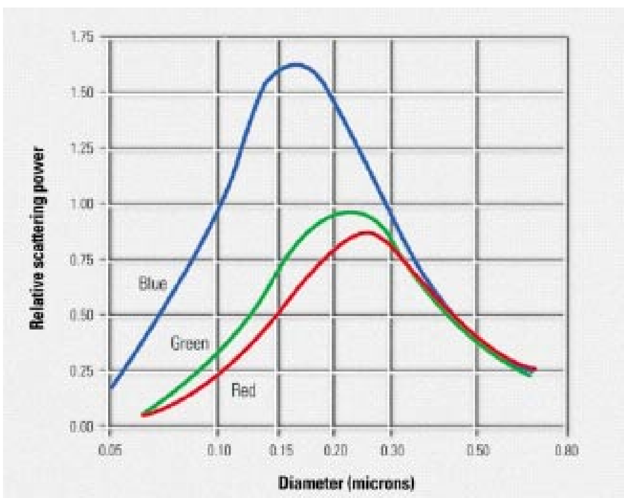

Figure **5**. Relationship between TiO_2 particle size and light scattering (Courtesy: Dupont Titanium Technologies).

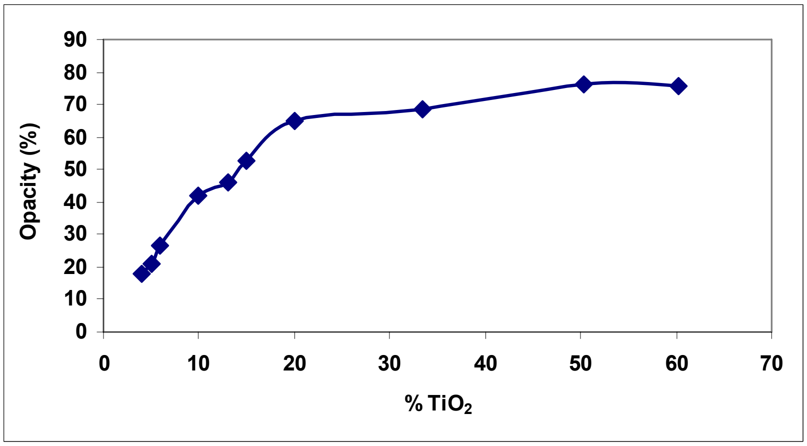

Figure **6**. Relationship between opacity and % TiO_2 loading in the ink.

The concentration of TiO_2 can affect the opacity of the cured film. Figure **6** shows the relationship between opacity and %TiO_2 in the ink. The opacity increases almost linearly until a TiO_2 content of 20% and then plateaus off. As the TiO_2 concentration increases, diffractive light scattering decreases because of TiO_2 particle overcrowding.

Settling Stability

One gauge of reliability in UV curable inkjet inks is resistance to settling. Settling of the ink is usually measured along with aging to determine if the particles agglomerate or flocculate. UV-curable inkjet inks that resist settling are highly desirable. It reduces preparation time before usage and hence agitation of ink before loading is not essential. Thus the ink may be left in the printhead for an extended period of time. This simplifies and expedites the start-up and the clean-up process.

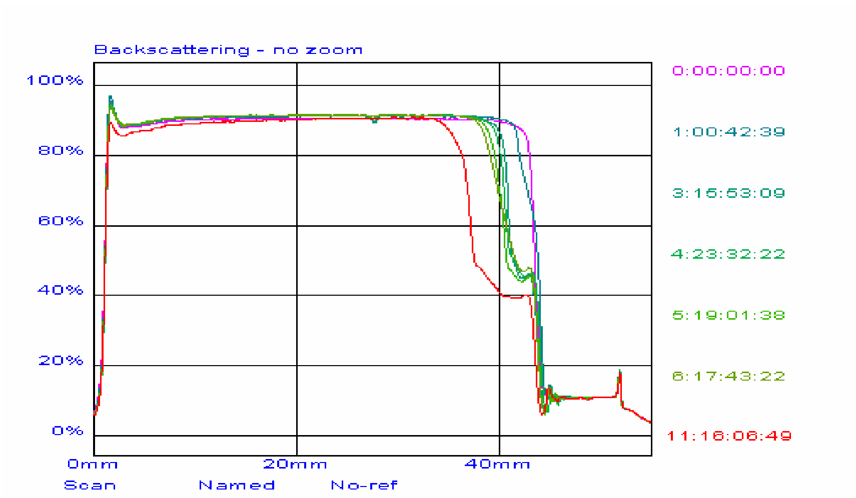

Figure **7**. Sedimentometry profile for the white ink stored at 60ºC. Measurements were collected using a Turbiscan LabExpert Sedimentometer.

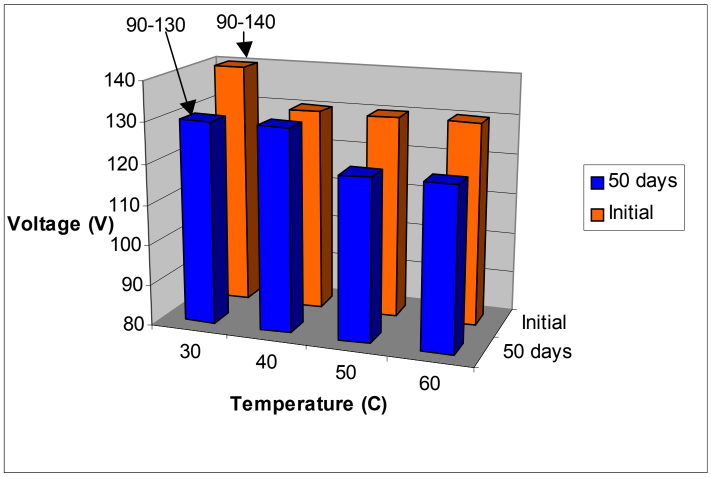

Figure **8**. Jet stability of white ink upon room temperature aging.

A key factor which leads to the settling of the white ink is the large density difference between the inorganic pigments and the ink vehicle. Figure **7** shows a representative aging profile for a white ink. The ink was aged at 60°C for an extended period of time. The overlay of the profiles is used to determine any pigment agglomeration. An ink is considered to have settled when the change in the backscattering is above 5%. The settling stability value obtained for the accelerated aged sample was converted to the equivalent stability at room temperature to obtain a stability of 50 days. It has to be pointed out that a gentle swirl, without the introduction of any air bubbles in the ink will maintain and extend settling shelf life. Particle size characterization also supports the finding that the inks remain stable over the time period.

In order to understand the significance of the sedimentometry results in realistic conditions, jet stability of the white ink was monitored by jet testing a white ink sample stored at room temperature using Spectra SE-128 printhead. Figure **8** shows the jet operating window for the 50 day aged sample versus the unaged sample. The results indicate no significant decrease in the jet operating window over the temperature range, indicating a very stable ink. Good settling stability for the white ink is an attractive option for the end user since there is no need to invest in special printhead equipment requiring stirring or agitation.

Conclusion

A UV curable white inkjet ink of low viscosity has been shown to have high opacity and settling stability with robustness in the printhead while also providing excellent end user properties on a wide variety of substrates.

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